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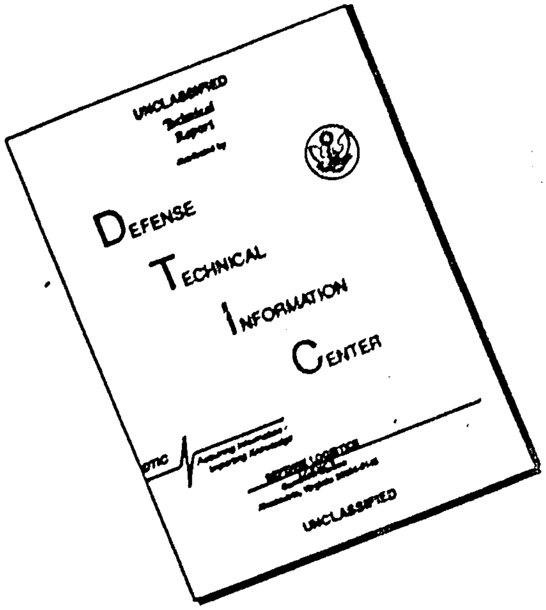

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THIRD BIMONTHLY PROGRESS REPORT

Covering the Period

1 August 1961 to 30 September 1961

TITLE: ACCELERATED DETERIORATION OF TEXTILES

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INTRODUCTION AND RELATIONSHIP TO PREVIOUS WORK

The previous report of this series was concerned primarily with the photooxidative degradation of cellulose, catalyzed by ferric ion. It was found that when cotton fabrics and sheets of cellophane, containing equal percentages of ferric ion, were exposed for equal lengths of time to radiation from a carbon arc in the Fadeometer, the cotton was more severely degraded than was the cellophane. (In these experiments degradation was measured as strength loss.) Current experimentation, described herein, has in part, been concerned with investigating this apparent difference between these two forms of cellulose. It is important to find out if cellophane, an easily studied material, is a valid model for cotton.

The previous report of this series also described the use of uranyl oxalate actinometers to measure, quantitatively, the light intensities to which the cellulose samples were exposed. Uranyl oxalate actinometers have now been used to measure not only incident light, but also the light transmitted and reflected by the cellulose samples. The techniques used, and data obtained are given in this report.

Also described in the current report are experiments using selected compounds other than those containing ferric ion which might act to accelerate the photooxidative degradation of cellulose.

SUMMARY

Possible reasons for the difference between cellophane and cotton, with regard to photooxidative degradation, were investigated as follows:

(1) It was expected that the cotton might absorb a longer fraction of the incident light than does the cellophane. Uranyl oxalate actinometers were used to measure, quantitatively, the amounts of light transmitted and reflected by the cellophane and cotton. It was found that a sheet of cellophane, containing 0.2% ferric ion, transmitted almost 85% of the incident light and reflected about 10% of the light. Thus, about 5% of the light was absorbed. A sheet of cotton

fabric containing 0.2% ferric ion transmitted about 15% of the incident light and reflected at least 15% of the light. The total reflectance from the cotton sheet is difficult to determine accurately because the light is reflected diffusely, scattered at all angles between 0° and 180°. Thus the cotton very probably did not absorb 70% of the incident light as indicated by the measurements above. It is probable, however, on the basis of other considerations, that the cotton did indeed absorb more light than the cellophane.

(2) It was also expected that the cotton might absorb more heat than the cellophane, and that the heat could accelerate degradation. Cotton and cellophane samples, impregnated to equal contents of ferric ion, were exposed to light in the Fadeometer at two different ambient air temperatures, 63° C. and 44° C. The cellophane was degraded to the same extent at both temperatures, but the cotton was degraded more at 63° C. than at 44° C. Even at 44° C., the cotton was degraded more than the cellophane. Whether this difference at 44° C. is still due partly to heat absorbed by the cotton, or is due to the greater amount of light absorbed, remains to be checked.

Work has been started using the following degradation accelerators other than ferric ion: ferrocene (dicyclopentadienyl iron), dicyclopentadienyl titanium dichloride, ceric ion, and cerous ion. In the limited experiments to date it has been found that cerium, applied to cotton either as cerous ion or as ceric ion, does promote photodegradation. At a 0.2% add-on on the cotton, cerium was about one-half as effective as ferric ion in reducing breaking strength.

FUTURE WORK PLANNED

1. Studies of degradation accelerators other than ferric ion will be continued. Combinations of two or more catalysts will be tried. It is possible that the combinations might act synergistically.

2. The major effort in the immediate future will be concerned with determining what chemical reactions are occurring in the cellulose when it is degraded photooxidatively in the presence of ferric ion catalyst. Cellophane will be used as the cellulose substrate since quantitative measurements of light absorbed by the cellophane can be made. From these data it should be possible to calculate quantum yields for the degradation reactions.

DETAILS

The cellophane and cotton used in these studies were the Avisco Type 300 cellophane and 80 x 80 print cloth described in the previous reports of this series. Samples were exposed to light in the Fadeometer as described in the 2nd Bimonthly Progress Report. The ambient air temperature in the Fadeometer was found to be 63° C. For some of the experiments described below the ambient air temperature was adjusted to an average of 44° C. by circulating room air through the Fadeometer cabinet. Actual temperatures in the cabinet ranged from 40° C. (at the inlet for the circulating air) to 47° C. in these runs. The uranyl oxalate actinometers, used to measure light intensities, have been described in the Second Bimonthly Report.

Transmittances of light through cotton and cellophane were determined, actinometrically, as follows:

Two actinometer cells were placed side by side in the Fadeometer with their windows (one square centimeter in area) facing the carbon arc and at a distance of 50 cm from the arc. A sheet of cotton or cellophane was mounted over the window of one cell so that all of the light entering the cell first passed through the sheet. The cells were then exposed to the carbon arc radiation for a selected time interval and then analyzed. From the analyses, the amounts of light absorbed by each cell were calculated and the percent of light transmitted by the sheet was calculated as:

$$\%\text{ light transmitted} = 100 \times \frac{\text{moles of light absorbed by cell with sheet over window}}{\text{moles of light absorbed by cell with uncovered window}}$$

The data for untreated cotton and cellophane, and for cotton and cellophane containing 0.2% ferric ion are given in Table 1.

Reflectances from cotton and cellophane were measured as follows:

The sample sheet was mounted at a 45° angle to the light incident from the carbon arc. An actinometer cell was mounted, at a distance of 6 cm. from the sheet, at a reflectance angle of 45°, so as to receive the light reflected from that section of the sheet which was 50 cm from the arc. A black shade on the actinometer cell limited the light entering the cell window to that reflected between the angles of 40° and 50°. A second (reference) actinometer cell was placed, facing the arc, at a distance of 50 cm, in order to determine the intensity of the light incident upon the sheet. The array was exposed to light, the cells analyzed, and the percent light reflected was calculated as:

$$\%\ \text{light reflected} = 100 \times \frac{\text{moles of light absorbed by reflectance cell}}{\text{moles of light absorbed by reference cell}}$$

The data are given in Table 1. In order to estimate whether the actinometer cells had measured the total amounts of light reflected, the reflectance patterns for cotton and cellophane were determined using a Goniophotometer. It was found that at an incident angle of 45° essentially all of the light was reflected from the cellophane between 40° and 50° (i.e. the light was specularly reflected). However, the reflectance from the cotton was diffuse. The maximum amount of light incident at 45° was reflected at 45°, but even at an incident angle of 0°, about 75% of this maximum value was reflected at 45°. It is apparent that the percent reflectance from cotton, measured actinometrically by the technique described above, and given in Table 1 is lower than the actual total reflectance. A more exact value for total reflectance has not yet been calculated.

Table 2 illustrates the effect of ambient air temperature in the Fadeometer cabinet on the rates of photodegradation in cotton and cellophane. The rate of degradation in the cellophane is apparently unaffected by temperature (in the range 44° C. to 63° C.), while the cotton, treated with ferric ion, is more severely degraded at the higher temperature.

In order to determine whether the cotton might be especially susceptible to the photocatalyzed degradation because it had been bleached, a sample of greige print cloth was obtained and exposed with the bleached cloth, under identical conditions. Table 3 illustrates that there was no difference between the greige and bleached cotton, impregnated with ferric ion.

Additional catalysts, other than ferric ion have been investigated on cotton. These were: ceric ion (applied as ceric nitrate solution); cerous ion (applied as cerous nitrate solution); ferrocene (dicyclopentadienyl iron), which was applied from a benzene solution; and dicyclopentadienyl titanium dichloride (applied from a chloroform solution). The latter two are of interest since they are volatile compounds which contain a cation which may be a potential catalyst. The data are given in Table 4. Included in the table, for comparison, are data for ferric ion. These experiments are now being extended to determine whether combinations of the catalysts might be more effective than the single catalysts. Additional catalysts are also being tried.

TABLE 1

ACTINOMETER MEASUREMENTS OF LIGHT TRANSMITTED THROUGH AND LIGHT REFLECTED FROM FERRIC ION TREATED COTTON PRINT CLOTH AND CELLOPHANE

Light source, Fadeometer arc

	Ferric ion in Sample, %	% of Light Transmitted	% of Light Reflected* (45° - 45°)
Cotton	0	24	22
	0.2	14	15
Cellophane	0	89	9
	0.2	84	11

*Actinometer was placed so as to receive the light reflected between 40° and 50°.

TABLE 2

PHOTODEGRADATION CATALYZED BY FERRIC ION

Strength Losses in Cotton and Cellophane at 44° C. and at 63° C. Ambient Fadeometer Temperatures.

Ferric Ion Concentration, %	Hours Exposure	% strength Loss in Cotton		% Strength Loss in Cellophane	
		44°	63°	44°	63°
0.2	36	57	76	30	34
0.1	36	25	72	20	0
0.05	36	22	56	Not tested*	0
0	36	10	13	0	0

*Not tested at 36 hours. Strength loss after 18 hours was 0%; Strength loss after 50 hours was 50%.

TABLE 3

PHOTODEGRADATION OF GREIGE AND BLEACHED PRINT CLOTH, CATALYZED BY FERRIC ION

Ferric ion content, 0.2%
Ambient temperature in the Fadeometer, 63°C.

Fabric	Hours Exposed in Fadeometer	% Strength Loss in Fabrics
Bleached	0	17
"	10	65
Greige	0	18
"	10	65

TABLE 4

PHOTOCATALYTIC DEGRADATION OF COTTON

Catalyst, %	Fadeometer Exposure	Fadeometer Temperature °C.	Loss in Breaking Strength, %
Ferric Ion, 0.2%	0	--	17
"	30	44	52
Ceric Ion, 0.2%	0	--	13
"	30	44	25
Cerous Ion, 0.2%	0	--	5
"	30	44	35
Ferrocene (0.2% iron equivalent)	0	--	0
" "	30	44	0
Dicyclopentadienyl titanium dichloride, 0.2% titanium equivalent)	0	--	0
" "	30	44	3